EQUATIONS OF STATE OF ORGANIC HIGH POLYMERS

P. S. Ku

General Electric Company
Philadelphia, Pennsylvania

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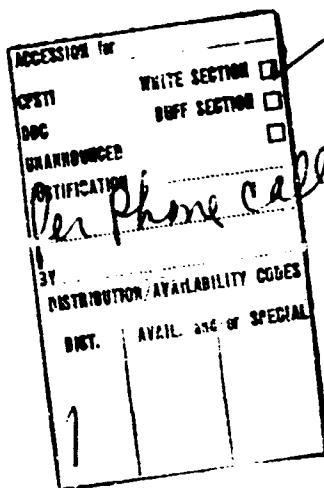
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SUMMARY THE TWO-PARAMETER SOLID EQUATIONS OF STATE, THE MURNAGHAN EQUATION, THE TAIT EQUATION, AND A GENERALIZED FORM OF THE BIRCH EQUATION WERE SELECTED TO FIT THE STATIC PRESSURE-VOLUME ISOTHERMS OF SOLID AND LIQUID HIGH POLYMERS. THESE EQUATIONS WERE FOUND TO HAVE A WIDE RANGE OF APPLICABILITY. THEY CAN BE EXTRAPOLATED TO VERY HIGH PRESSURE WITH GOOD ACCURACY. THE FIRST AND SECOND DERIVATIVES APPEAR TO BE WELL BEHAVED. THESE EQUATIONS CAN BE USED TO OBTAIN ANALYTICAL EXPRESSIONS FOR THE GRÜNEISEN PARAMETER, CONTAINING THE VOLUME OR PRESSURE EXPLICITLY AND TEMPERATURE IMPLICITLY. THEY YIELD VALUES THAT SEEM TO BE IN AGREEMENT WITH THE LATEST THEORETICAL DEDUCTIONS. WHEN USED WITH THE KENNEDY FUSION LAW, THESE ISOTHERMAL EQUATIONS CAN BE USED TO PREDICT MELTING TEMPERATURES UNDER VERY HIGH PRESSURES. IT HAS ALSO BEEN SHOWN THAT THESE EQUATIONS CAN BE USED TO PREDICT THE SHOCK COMPRESSION DATA, AND A DISCUSSION OF THE SHOCK COMPRESSION DATA AS INFLUENCED BY THE DEGREE OF CRYSTALLINITY OF THE POLYMERS IS GIVEN. ALONG WITH THE PVT PROPERTIES OF POLYMERS, THE SPECIFIC HEATS (C_P AND C_V) OF POLYETHYLENE, POLYCHLOROTRI-FLUOROETHYLENE, AND POLYTETRAFLUOROETHYLENE UNDER HIGH PRESSURES ARE EVALUATED.

KEY WORDS MURNAGHAN EQUATION, TAIT EQUATION, MODIFIED BIRCH EQUATION, MIE-GRÜNEISEN EQUATION, SIMON EQUATION, KENNEDY FUSION EQUATION, HUGONIOT.

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SUMMARY

The two-parameter solid equations of state, the Murnaghan Equation, the Tait Equation, and a generalized form of the Birch Equation were selected to fit the static pressure-volume isotherms of solid and liquid high polymers. These equations were found to have a wide range of applicability. They can be extrapolated to very high pressure with good accuracy. The first and second derivatives appear to be well behaved. These equations can be used to obtain analytical expressions for the Grüneisen parameter, containing the volume or pressure explicitly and temperature implicitly. They yield values that seem to be in agreement with the latest theoretical deductions. When used with the Kennedy fusion law, these isothermal equations can be used to predict melting temperatures under very high pressures. It has also been shown that these equations can be used to predict the shock compression data, and a discussion of the shock compression data as influenced by the degree of crystallinity of the polymers is given. Along with the PVT properties of polymers, the specific heats (C_P and C_v) of polyethylene, polychlorotrifluoroethylene, and polytetrafluoroethylene under high pressures are evaluated.

1. INTRODUCTION

There is considerable theoretical and practical interest in studying the equations of state of
solids under high pressure. For high polymers, there are only scattered data available in
the literature including the pioneering work by Bridgman. A common method of
correlating the data has been the use of a polynomial--the specific volume as a
function of ascending powers of pressure. The obvious disadvantage of this method is that
the empirical equation of state is limited by the range of the experimental data. Extrapolation
beyond the range becomes highly uncertain; however, extrapolation is sometimes necessary
for estimating the pressure-volume relationship in the region where no experimental data
exists. There is no theoretical approach which yields results for high polymers which
compare in accuracy to the experimental data.

It has been shown[1] that the bulk properties of organic high polymers under high pressures
behave similarly to the properties of other non-metallic and metallic solids. These properties
under high pressure can be well represented by one of the several semi-empirical equations
of state which can be derived on the basis of the theory of finite strains. Among these
equations, the Murnaghan and Birch equations are well known. Anderson[2] has shown that
the Murnaghan equation can be used to estimate P-v isotherms to very high pressures many
times beyond the pressure range where the parameters were determined with good accuracy.
The simplest form of the Birch equation has two fixed exponents and one adjustable coefficient.
A generalized and modified form of the Birch equation based on the theory of finite strains
containing two adjustable parameters was used in the present paper. The Tait equation,
also a two-parameter equation of state, has customarily been used to correlate compression
data for liquids. Nanda and Simha[3] have applied the Tait equation to solid and liquid organic
high polymers. MacDonald[4] has applied the Tait equation to other solids and compared the
Tait and Murnaghan equations.

These three equations have been chosen to fit the volumetric data of several organic high polymers. The volumetric data used were taken from the work of Weir[5] and Hellwege, Knappe, and Lehmann[6]. Weir's data were taken at pressures up to 10,000 atm.; while those of Hellwege et al. cover a wide temperature range encompassing both solid and liquid regions of the polymers.

It was found that these three equations could be extrapolated to very high pressures with good accuracy. Values of the first and second derivatives obtained from these equations appear to be smooth, well behaved, and in good agreement with the values obtained from other methods.

On the basis of the above results, four areas were examined:

a. The specific heats C_p and C_v under high pressures for three polymers were evaluated.

b. The melting phenomena of polymers under high pressure are examined on the basis of the Simon Equation and the Kennedy fusion law. When combined with the Kennedy fusion law, these isothermal equations of state can predict the melting temperature of polyethylene up to 30,000 atmospheres and agree to within 10 percent with the experimental data.

c. The Grüneisen parameter can be directly calculated from these equations of state by invoking one of the well known models of solids. Values thus obtained seem to be in good agreement with the latest theoretical deductions.

d. The shock compression of polymers is shown to be predictable. The few Hugoniots found in the literature are examined, and it is found that in all cases insufficient information is given on the physical properties of the polymers and the initial conditions of the experiments, which are important in the calculation of Hugoniots. The observed decrease in slope of the Hugoniots at high shock pressures may be explained by the opposite effects of pressure and temperature on the degree of crystallinity of the polymers.

The wide range of applicability of these equations of state seems to indicate a fruitful area for theoretical and experimental investigation.

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2. ISOTHERMAL EQUATIONS OF STATE

The Murnaghan, Tait and a generalized form of the Birch equation have been chosen to fit the experimental data. The Murnaghan equation can be derived from the fact that the bulk modulus of some solids is a linear function of pressure along an isotherm,

$$-v \left(\frac{\partial P}{\partial v} \right)_T = B_o + sP \tag{1}$$

where v and P indicate the specific volume and the pressure, respectively; B_o is the initial bulk modulus at atmospheric pressure, and s is a dimensionless coefficient.

The Murnaghan equation is obtained by integrating Equation 1 with the pressure given as a function of (v_o/v),

$$P = \frac{B_o}{s} \left[\left(\frac{v_o}{v} \right)^s - 1 \right] \tag{2}$$

Anderson[2] has shown that the Murnaghan equation is capable of predicting the compression of solids to very high pressures. He further demonstrated that the necessary parameters can be obtained from ultrasonic measurements. Because of the inherent inaccuracy in the direct measurements of specific volume and the small change of volume under pressure, it is very difficult to obtain B_o and B from the slopes of the P-v isotherm, especially when the pressure interval is large.

In the original Birch equation, the exponents of the v_o/v terms had the fixed values of 7/3 and 5/3. Because of its greater flexibility, a modified and generalized form of the Birch Equation given by Knopoff[7] is preferred. In this equation, the pressure is given as

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$$P = \left|3K_o/2\,(1 + a_2)\right|(v_o/v)^{2(1+a_2)/3}\left[(v_o/v)^{2(1+a_2)/3} - 1\right] \tag{3}$$

where $K_o = -v\,(\partial P/\partial v)_T$ at $P = 0$, a_2 is the coefficient of the quadratic term in the strain energy expressed as a function of strain, and P and v have the usual meanings. If Equation 3 is rearranged, and $3 K_o/2\,(1 + a_2)$ and $3/2\,(1 + a_2)$ are considered as two adjustable parameters, the following equation is obtained

$$v/v_o = \left[1/2 + (P/A' + 1/4)^{1/2}\right]^{-B'} \tag{4}$$

with $A' = 3K_o/2\,(1 + a_2)$ and $B' = 3/2\,(1 + a_2)$.

The Tait Equation is purely empirical. It has been used extensively to represent the P-v isotherms of liquids. Recently the Tait Equation has been applied to polymers and other solids[3,4]. This equation can be written as

$$v/v_o = 1 - A\,\ln\left[(B + P)/(B + 1)\right] \tag{5}$$

In Equation 5, A and B are the two adjustable parameters. The constant A is often regarded as a universal constant. Nanda and Simha[3] have taken this view and apply the constant A found for hydrocarbons to polymers. In order to obtain a good fit, both parameters have been considered as adjustable in the present work. It is found that the variation of A is rather large near the glassy transition temperature in the case of polymethyl methacrylate.

An attempt has been made to fit these equations to the experimental data by means of the method of least squares. The general method, developed by Deming[8], which is applicable to non-linear equations, was not found to be helpful in this case. It seems to require that the initial estimate of the values of the parameters be very close to the true values in order that

the linearization of the expressions for the errors be valid. Consequently, an iteration procedure was developed. First, a pair of initial values of the parameters are obtained from a pair of well separated data points. Then the sum of error squares is minimized by trial and error with respect to each parameter alternately, with the other parameter held constant. The minimum is of the order of 10^{-6} for Weir's high pressure data. It is in the order of 10^{-7} for the data of Hellwege et al. The sum of error squares becomes larger as the melting point is approached. In the case of polyethylene in the melting region (where the volume change is rather sudden), fitting of the data could only be done by obtaining separate parameters for the liquid and solid phases.

Tables 1, 2, and 3 give the parameters in the Murnaghan, modified Birch, and the Tait equations. Temperature dependence of the parameters in each of the equations in the case of polymethyl methacrylate are plotted in Figures 1, 2, and 3. The parameter B_o in the Murnaghan Equation, the parameter K_o in the modified Birch Equation, and B in the Tait Equation are always decreasing with increasing temperature as expected. Both coefficients s (Murnaghan Equation) and a_2 (Birch Equation), which are related to the compressibility, remain fairly constant at temperatures far below the transition temperature and then rise and fall precipitously on going through the transition.

The parameter s in the Murnaghan equation for solid and liquid atactic (amorphous) polystyrene is plotted in Figure 4. The shape of the curve for the parameter s is similar to that of the specific heat data of Karasz, Bair, and O'Reilly[9]. The cause of the abrupt rise of s near 250°C is not clear. Nanda and Simha[3] suspect degradation or loss of material at this high temperature.

Any of the three equations of state can be used to calculate the specific volumes of polymers with higher accuracy than can Weir's polynomials, even in the range where the polynomials were fitted to accurately represent the experimental data. In Table 4, the specific volumes of polytetrafluoroethylene at 30°C and at pressures from 1000 to 10,000 atmospheres are compared with values calculated from the Murnaghan, Birch, Tait, and the polynomial

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Table 1. Parameters in the Murnaghan Equation of State for High Polymers

Polymer	B_o (atm)	S	v_o	$T \; (^{\circ}K)$	Static Pressure Range (atm)
Low Density Polyethylene	30063.2 25138.4	9.4902 8.4305	1.0895 1.1269	293.2 343.2	10,000 10,000
High Density Polyethylene	40148.4[a] 35034.6[a]	16.9992 12.2738	1.028 1.042	292.6 332.8	2,000[a] 2,000[a]
Polymethyl Methacrylate	39712.3[a] 28191.3[a]	9.0004 10.9414	0.842 0.862	293.2 373.2	2,000[a] 2,000[a]
Polystyrene	36388.4[a] 14073.2[a]	8.5179 15.7109	0.955 0.994	293.2 399.2	2,000[a] 2,000[a]
Polychloro-trifluoroethylene	39146.6 33993.5	10.4331 9.8502	0.4662 0.4745	293.2 343.2	10,000 10,000
Polytetrafluoro-ethylene	29267 21040	14.9218 12.8603	0.4484 0.4484	293.2 293.2	1 to 5,000 6,000 to 10,000
Polyvinyl Fluoride	41687.7 31102.5	7.8864 9.3506	0.7956 0.8135	293.2 343.2	10,000 10,000
Polyvinylidene Fluoride	34757.8 32208.2	9.5880 9.3077	0.6439 0.6582	293.2 343.2	10,000 10,000
Polyvinyl Alcohol	58233.0 46258.8	10.7629 11.0647	0.7720 0.7861	293.2 353.2	10,000 10,000
Nylon 6-6* Nylon 6-10	56688.2[a] 55470.7[a]	7.7507 7.8852	0.858[b] 0.917	300 300	40,000[a] 40,000[a]

(a) the unit is in Kg/cm^2

(b) Based on average density of amorphous and crystalline samples.

Table 2. Parameter in the Modified Birch Equation of State for High Polymers

Polymer	K_0 (atm)	a_2	Temperature ($^\circ$K)
Low Density Polyethylene	27861.4 22116.0	4.77267 3.83297	293.2 353.2
High Density Polyethylene	42770.0 [a] 9063.7	7.0998 10.1728	292.6 403.3
Polymethyl Methacrylate	39813.9 [a] 27704.4	3.54545 5.08729	293.2 373.2
Polystyrene	36284.7 [a] 17976.6	3.43000 8.9575	293.2 373.8
Polychloro-tri-fluoroethylene	39359.3 31664.9	4.55555 4.97655	293.2 353.2
Polytetrafluoro-ethylene	27741.8 18801.6	7.7944 7.0129	293.2 (0 – 5000 atm) 293.2 (5000 – 10000 atm)
Polyvinyl Fluoride	39714.1 29396.5	3.64910 4.54066	293.2 343.2
Polyvinyl Alcohol	57311.2 49088.0	4.93094 4.25164	203.2 353.2
Nylon 6-6 (oriented) Nylon 6-6 (unoriented) Nylon 6-10	52578.3 [a] 62392.7 [a] 50865.7 [a]	3.69220 3.56303 3.83297	300 300 300

(a) The unit of K_0 is in Kg/cm^2

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Table 3. Parameters in the Tait Equation of State for High Polymers

Polymer	A	B (atm)	Temperature ($^\circ$K)
Low Density Polyethylene	0.086812 0.097213	2510.1 2383.0	293.2 343.2
High Density Polyethylene	0.055221 0.054046	2310.9[a] 1809.7	292.6 332.8
Polymethyl Methacrylate	0.098701 0.080562	3911.7[a] 2253.7	293.2 373.2
Polystyrene	0.090000	3200.0[a]	293.2
Polychloro-trifluoroethylene	0.086480 0.084714	3430.0 2777.4	293.2 353.2
Polytetrafluoro-ethylene	0.05587 0.06367	1523.5 1216.8	293.2 (1 to 5000 atm) 293.2 (6,000 to 10,000 atm)
Polyvinyl Fluoride	0.10650 0.088401	4400.0 2656.8	293.2 353.2
Polyvinylidene Fluoride	0.088353 0.090014	3019.4 2834.2	293.2 343.2
Polyvinyl Alcohol	0.081121 0.077595	4676.8 3513.8	293.2 353.2

(a) The unit of B is in Kg/cm^2
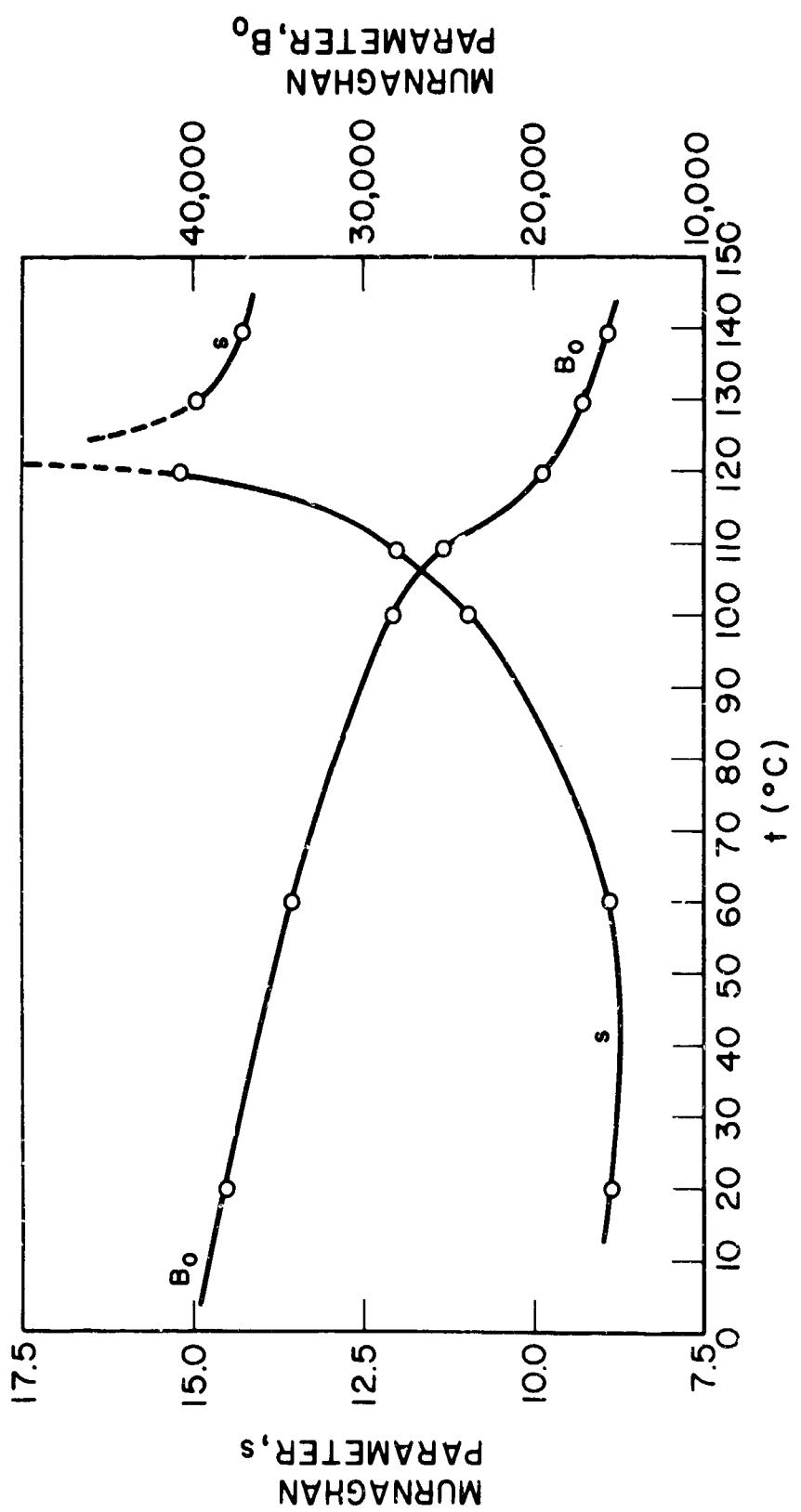
Figure 1. Parameters s (Left Scale) and B_0 (Right Scale) in the Murnaghan Equation of State for Polymethyl Methacrylate

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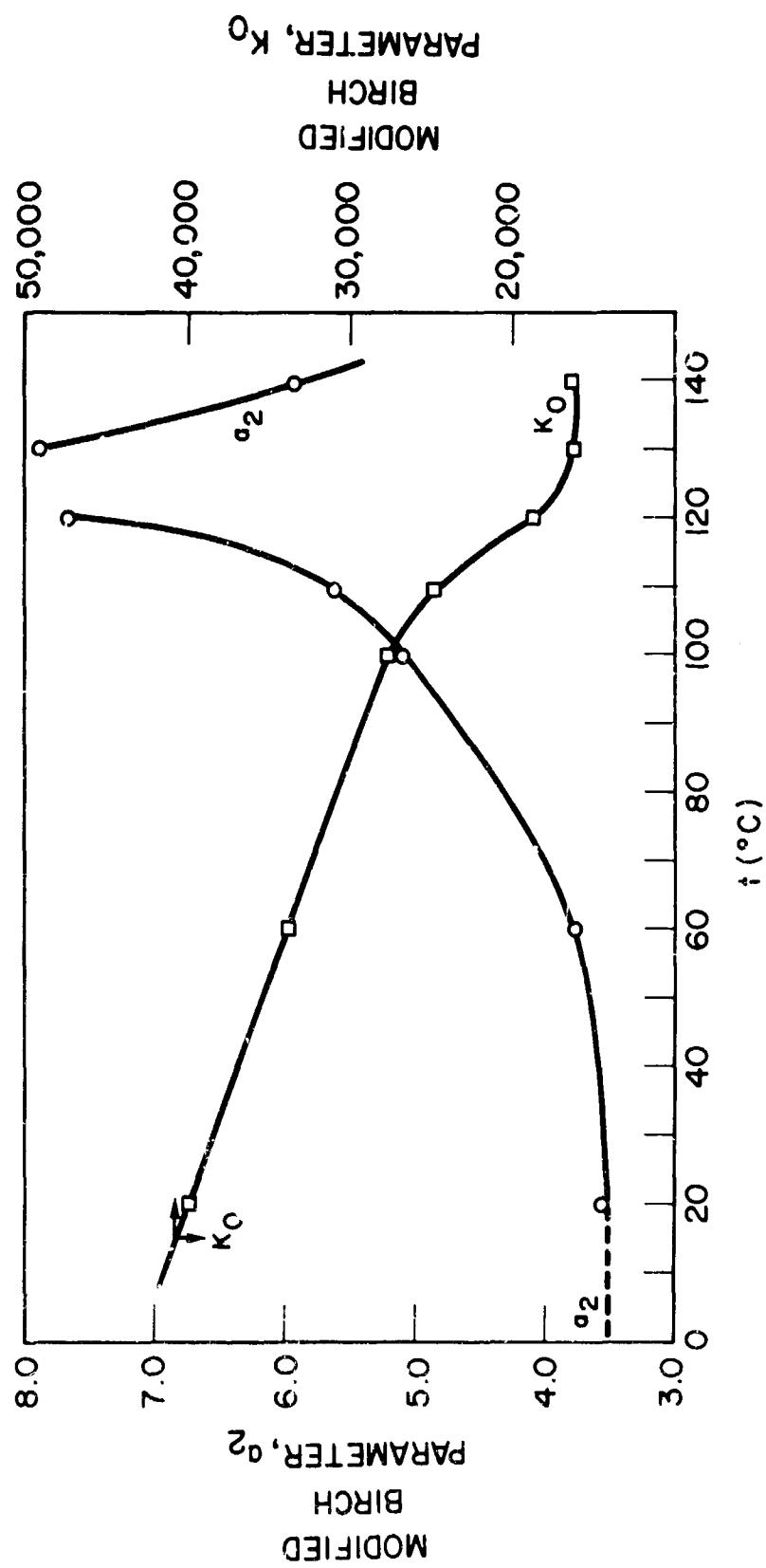
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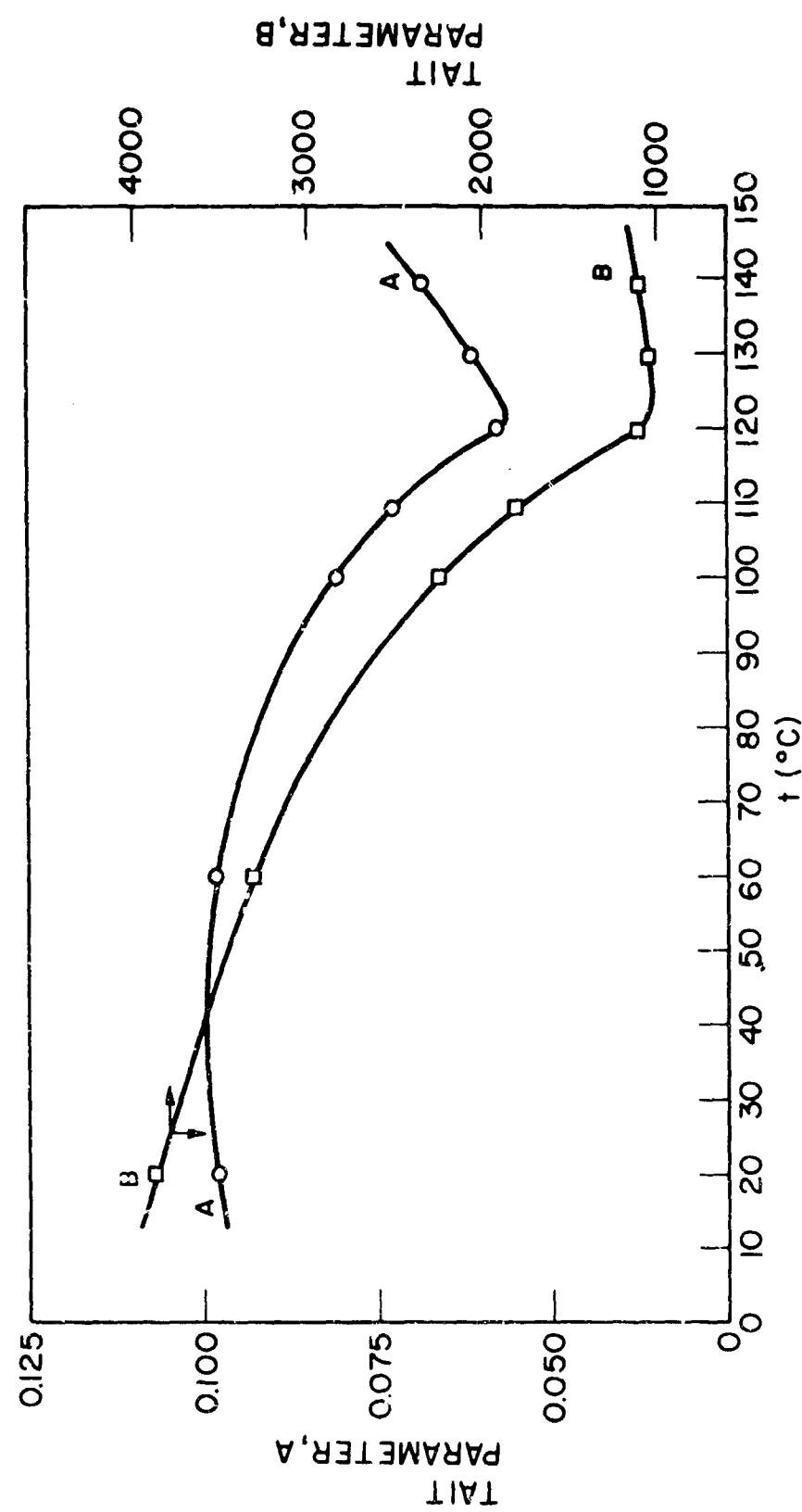
Figure 3.   Parameters A (Left Scale) and B (Right Scale) in the Tait Equation of State for Polymethyl Methacrylate

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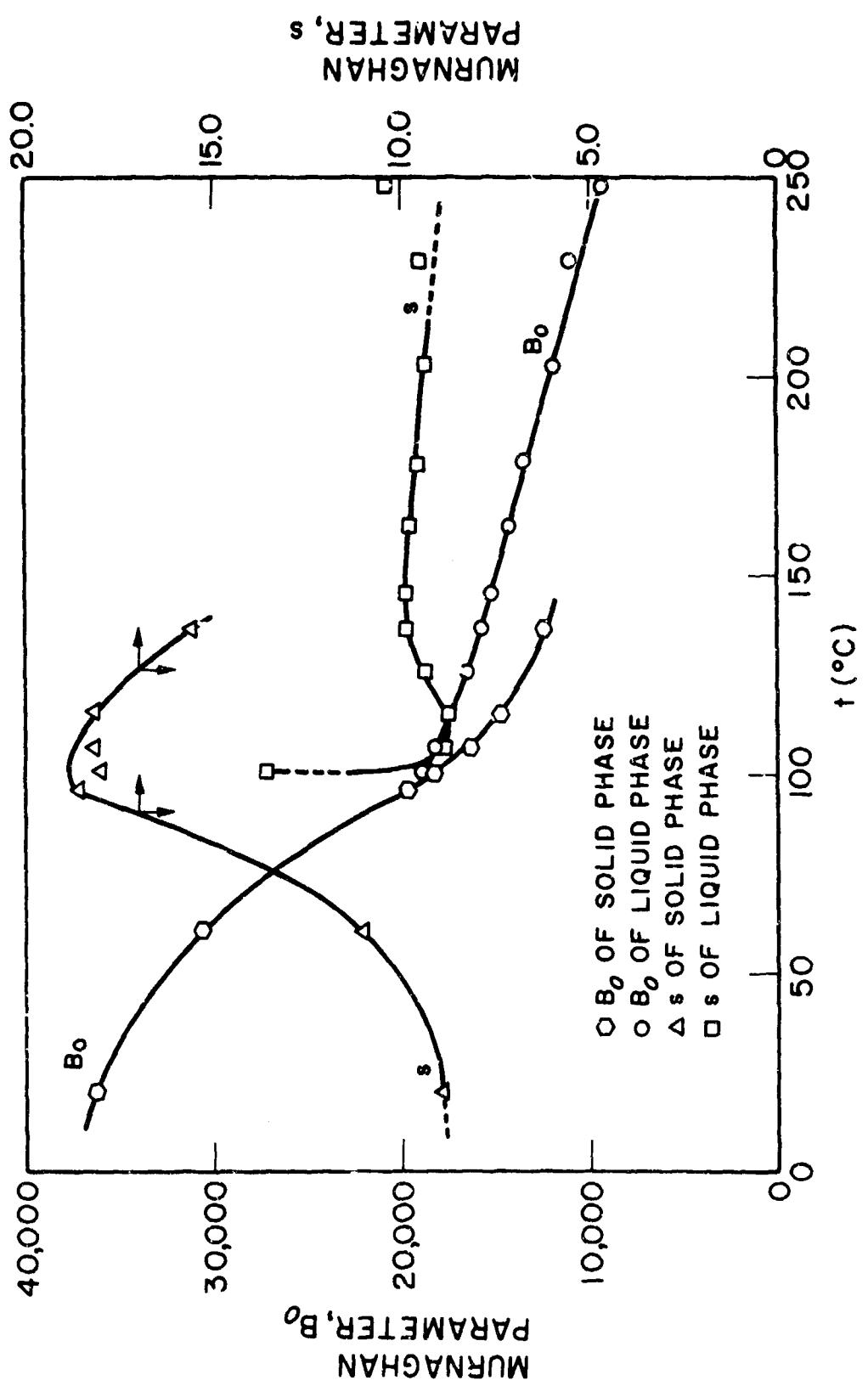
Figure 4. Parameters B_0 (Left Scale) and s (Right Scale) in the Murnaghan Equation of State for Solid and Liquid Polystyrene

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Table 4. Comparison of Specific Volumes (cm^3/g) of Polytetrafluoroethylene at $30^{o}C$ with the Calculated Values by Polynominal, Murnaghan, Birch, and Tait Equations of State

P, atm	Expt'l	12-parameter Polynominal	Murnaghan	Birch	Tait
1000	0.4367	0.4397	0.4376	0.4373	0.4374
2000	0.4289	0.4308	0.4286	0.4284	0.4285
3000	0.4228	0.4219	0.4221	0.4221	0.4220
4000	0.4174	0.4181	0.4170	0.4171	0.4170
5000	0.4120	0.4134	0.4128	0.4130	0.4129
6000	0.3985	0.3981	0.3983	0.3982	0.3981
7000	0.3942	0.3921	0.3944	0.3944	0.3944
8000	0.3907	0.3905	0.3910	0.3910	0.3910
9000	0.3879	0.3876	0.3880	0.3880	0.3880
10000	0.3856	0.3855	0.3853	0.3853	0.3853

equations of state. In the transition region (1000 to 5000 atmospheres), all the three isothermal equations give more accurate predictions than does Weir's 12-parameter polynomial. Even in the range 6000 to 10,000 atmospheres where the polynomial fits the data very well, these equations are still more accurate.

The compression data (v/v_o) of polyethylene and polystyrene up to 40,000 Kg/cm^2, published by Bridgman[10], are compared in Table 5 with values calculated from the generalized Birch equation. The parameters used in the calculations were evaluated by fitting the data of Hellwege et al. up to only 2000 Kg/cm^2. The agreement might have been better, if the "room" temperature of Bridgman's experiment had been specified. In this calculation $20^{\circ}C$ has been used.

The derivatives of these equations yield smooth and reasonable values. The compressibility of polyethylene at $20^{\circ}C$ is calculated by means of the Murnaghan equation and compared to that obtained from graphical differentiation of the P-v isotherm and with the compressibility calculated from the polynomial equation. This comparison is given in Figure 5.

Table 5. Comparison of Calculated (by Birch Eq.) v/v_o of Polyethylene, Polystyrene up to 40,000 Kg/cm^2 with Bridgman's Experimental[10] Results

| Pressure	Polyethylene			Polystyrene		
P (Kg/cm^2)	v/v_o (calc.)	v/v_o (Expt'l)	% Dev.	v/v_o (calc.)	v/v_o (Expt'l)	% Dev.
2500	0.9378	0.9447	0.73	0.9473	0.9591	1.23
5000	0.9025	0.9126	1.11	0.9125	0.9273	1.63
10000	0.8582	0.8681	1.14	0.8656	0.8800	1.64
15000	0.8293	0.8379	1.03	0.8334	0.8481	1.73
20000	0.8078	0.8148	0.86	0.8090	0.8244	1.87
25000	0.7907	0.7960	0.66	0.7893	0.8054	2.00
30000	0.7766	0.7806	0.51	0.7728	0.7894	2.10
35000	0.7646	0.7679	0.44	0.7587	0.7760	2.23
40000	0.7541	0.7570	0.39	0.7464	0.7641	2.32
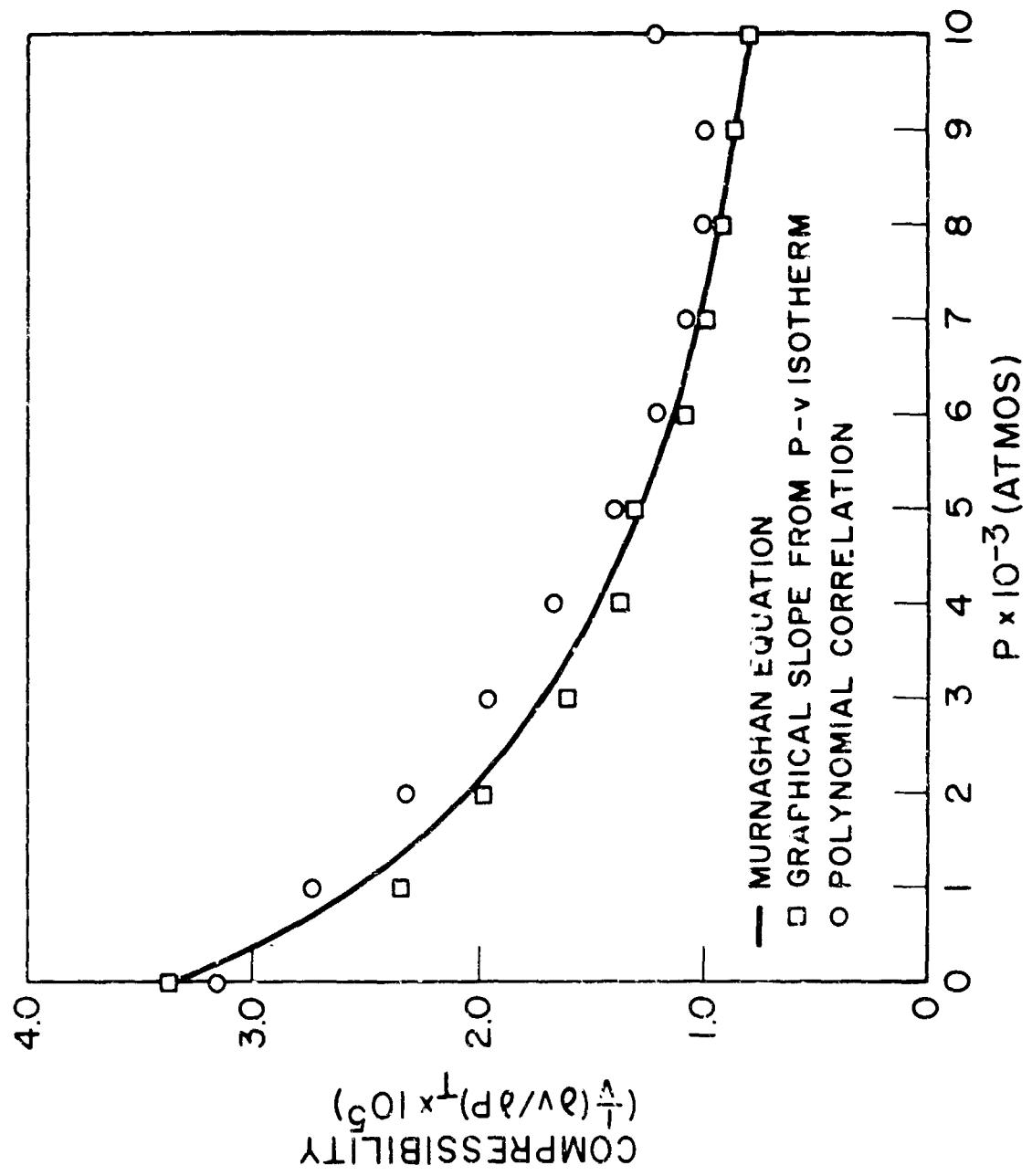
Figure 5. Comparison of Calculated Compressibility of Polyethylene with Values Obtained from Graphical Slope and Values Calculated from Polynomial Empirical Equation of State

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3. SPECIFIC HEATS OF HIGH POLYMERS UNDER HIGH PRESSURES

The thermodynamic expression for the variation of C_P with pressure and the relationship between C_p and C_v are well known. They are given as,

$$C_P (P) = C_P (P = 0) - T \int_0^P (\partial^2 v / \partial T^2)\, dP \qquad (6)$$

and

$$C_P (P) - C_v (P) = T v \alpha^2 / \beta \qquad (7)$$

where α, and β are the thermal expansion coefficient and the compressibility, respectively. The quantitives P, T, C_p, C_v, and v have the usual meanings. The thermal expansion coefficient α and the second derivative of volume with respect to T for branched polyethylene, polytetrafluoroethylene, and polychlorotrifluoroethylene can be obtained as a function of P from the polynominal equations by Weir[5].

The volumetric data reported by Hellwege et al.[6] have only three significant figures. Since the thermal expanison coefficient is in the order of 10^{-4}, it is difficult to obtain reasonable values of this quantity $(\partial \ln v / \partial T)_P$ and of $(\partial^2 v / \partial T^2)_P$. At the present time, the specific heat of polystyrene and polymethyl methacrylate under high pressure cannot be obtained from equations (6) and (7).

The specific heats of many high polymers have been measured under atmospheric pressure. In Table 6 there are assembled the data sources, types of material, and the range of measurements of several polymers which are of the most interest in this work.

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Table 6. Data Sources of Specific Heat (C_p) of High Polymers under Atmospheric Pressure

Polymer	Type of Polymer	Temperature Range	Ref
Polyethylene	Linear and branched	90° to 433^oK	(11)
Polyethylene	Annealed, drawn, granular and sheet	-20° to 200^oC	(12)
Polyethylene	Low pressure	53° to 145^oC	(13)
Polychloro-trifluoroethylene	Quenched and slow cooled	0° to 240.8^oC	(14)
Polytetrafluoro-ethylene	Powdered and quenched Powered and drawn	346° to 725^oK -25° to 120^oC	(15) (16)
Polytetrafluoro-ethylene	Commercial sheet sample	-130° to 80^oC	(17)
Polymethyl Methacrylate	(Data by Sochava, et al)	10° to 300^oK	(18)
Polyvinyl Alcohol	(Data by Sochava, et al)	10° to 245^oK	(19)
Polystyrene	Isotactic	0° to 310^oK	(20)
Polystyrene	Atactic-annealed, as received Isotactic-amorphous, annealed	293° to 378.61^oK 89.43^o to 473.14^oK 301.9^o to 521.4^oK 305° to 526^oK	(9) (9) (9) (9)
Polystyrene	Atactic and isotactic	-50° to 280^oC	(21)
Polyvinyl Chloride	With 10, 20, 30% plasticizer	-30° to 80^oC	(17)
Polyvinyl Chloride	Powdered GE L-38	-20° to 120^oC	(22)

The specific heats C_p and C_v under pressures up to 10,000 atmospheres, have been obtained for polyethylene, polychlorotrifluoroethylene, and polytetrafluoroethylene from Weir's polynominals. They are presented graphically in Figures 6 through 12.

In Figures 6 and 7, the specific heat of polyethylene is plotted as a function of temperature and as a function of pressure. Some errors in the values of the specific volumes of polyethylene were found in Weir's data between 1 and 2000 atmospheres and above 60°C. These errors have been corrected by comparison with the data of Hellwege et al. The material used by Weir was a brached type polyethylene which has a melting point of about 110°C. The atmospheric specific heat C_p of this material has been measured by Dole et al[11]. This data has been used in the C_p (0) in Equation (7) to obtain the C_p's shown in Figures 6 and 7.

The effect of pressure on C_p, i.e., $T \int_0^P (\partial^2 v / \partial T^2)_P \, dP$ for polytetrafluoroethylene and polychlorotrifluoroethylene are in the order of 10^{-4} and 10^{-3}, respectively. Compared to the magnitude of the specific heat itself, this effect is negligible.

The quantity $(C_p - C_v)$ of polytetrafluoroethylene is plotted as a function of temperature in Figure 10. Two first order transitions have been reported between 10 and 40°C and 1 and 6,000 atmospheres. This transition is reflected in the $(C_p - C_v)$ values. Above 6,000 atmospheres $(C_p - C_v)$ becomes very small.

The quantity $(C_p - C_v)$ for polychlorotrifluoroethylene (Kel-F) as a function of temperature and of pressure is plotted in Figures 11 and 12, respectively. Figure 11 shows that $(C_p - C_v)$ is linear in temperature up to 9,000 atmospheres. In Figure 12, the three isotherms cross each other twice, once between 3,000 to 4,000 atmospheres and once near 8×10^3 atmospheres. The one atmosphere curve does not show an effect of the glass transition at 52°C and one atmosphere which has been confirmed by Hoffman and Weeks[23].

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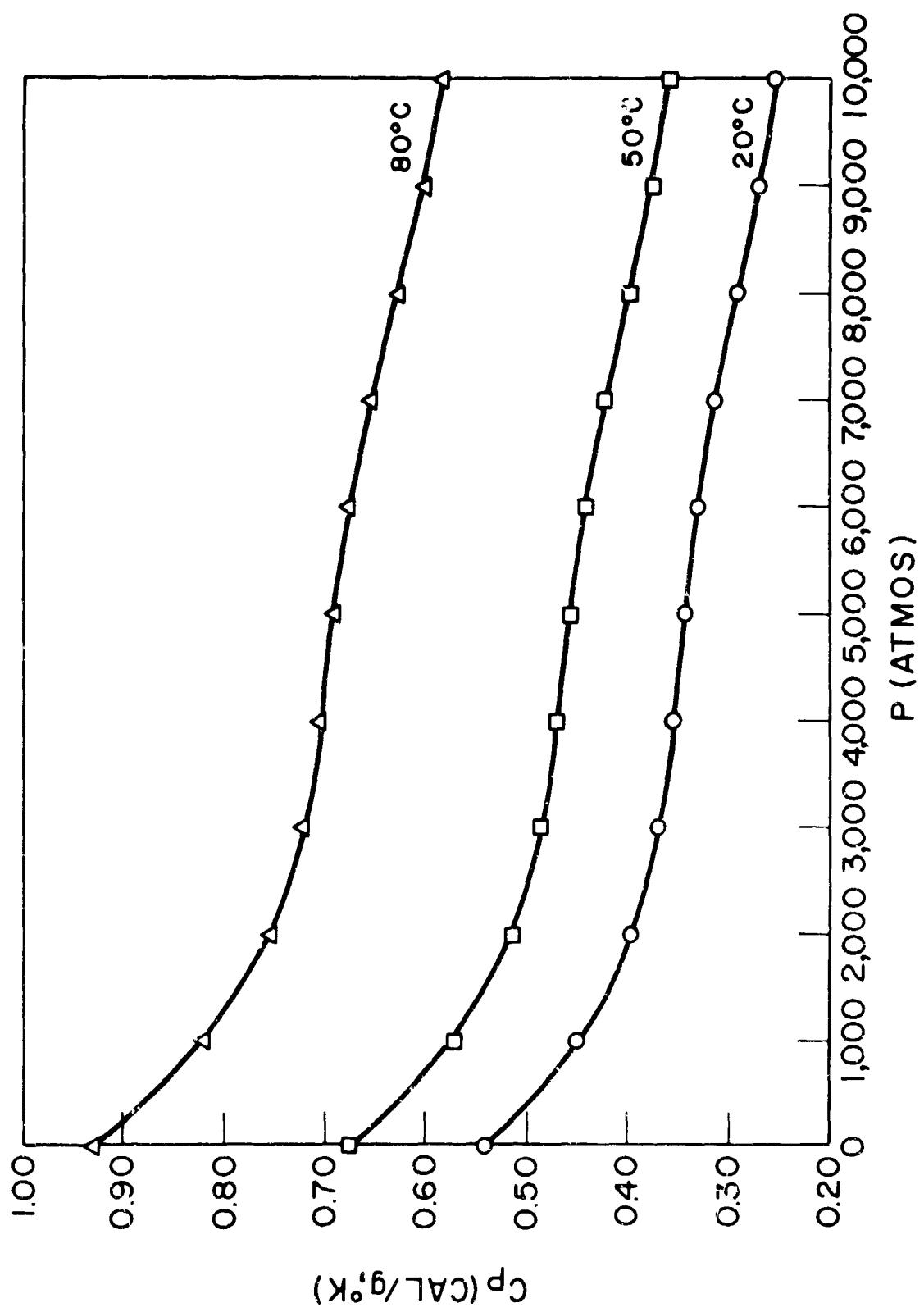
Figure 6. Pressure Dependence of the Specific Heat, Cp of Polyethylene (low density) at Constant Temperatures
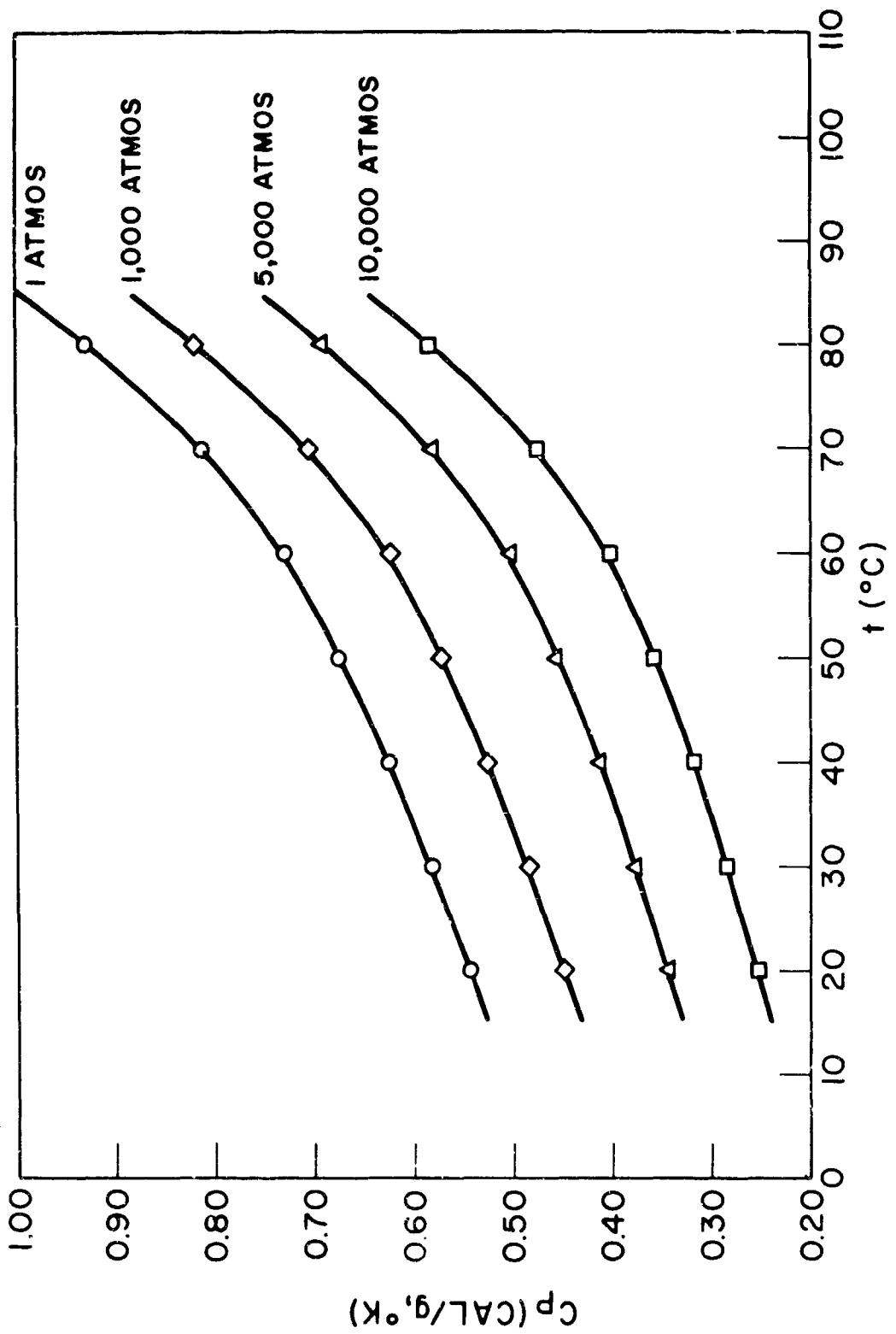
Figure 7. The Specific Heat, C_p of Polyethylene Under High Pressures as a Function of Temperature Along Isobars
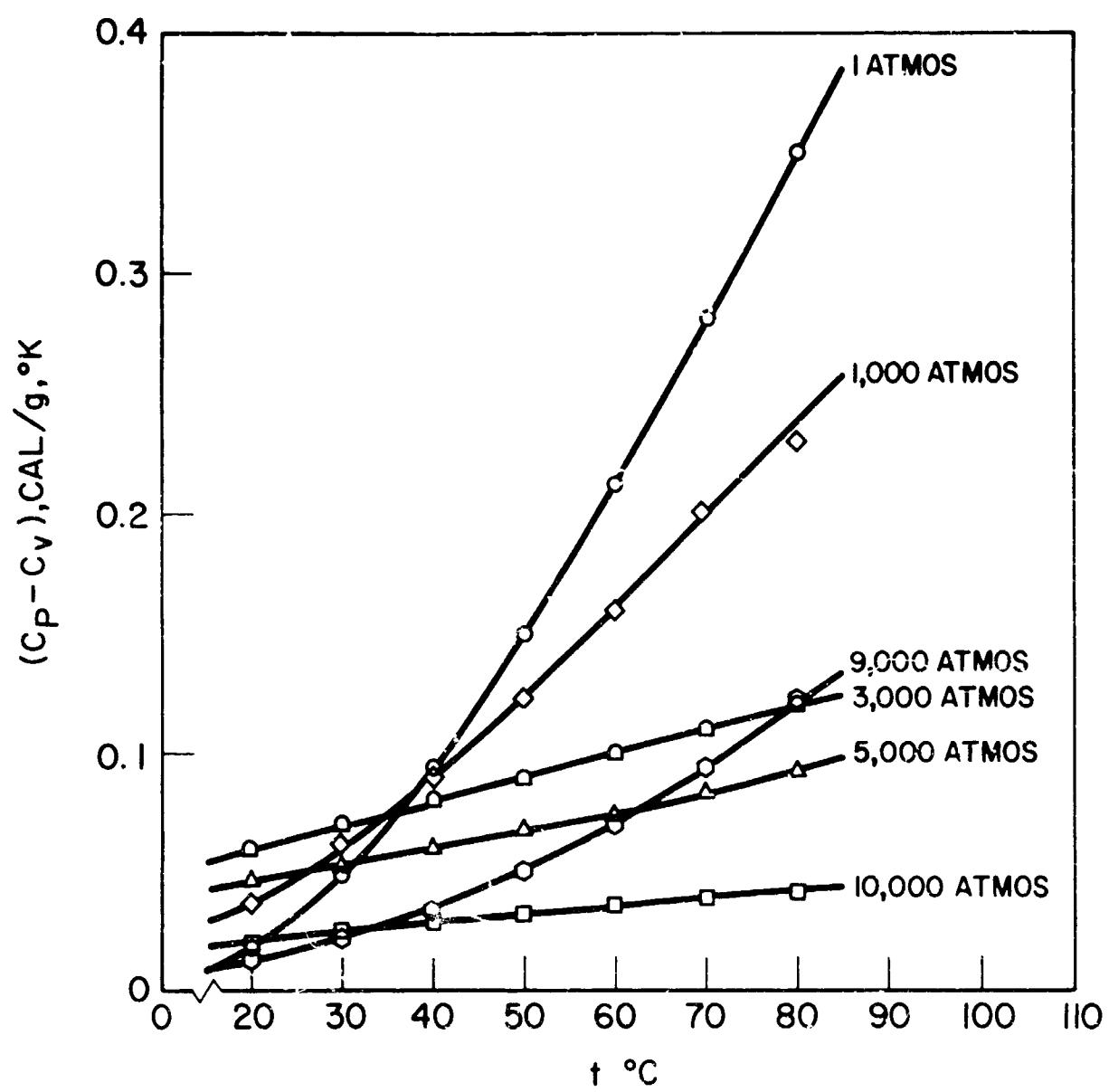
Figure 5. Temperature Dependence of $(C_p - C_v)$ of Polyethylene Along Isobars
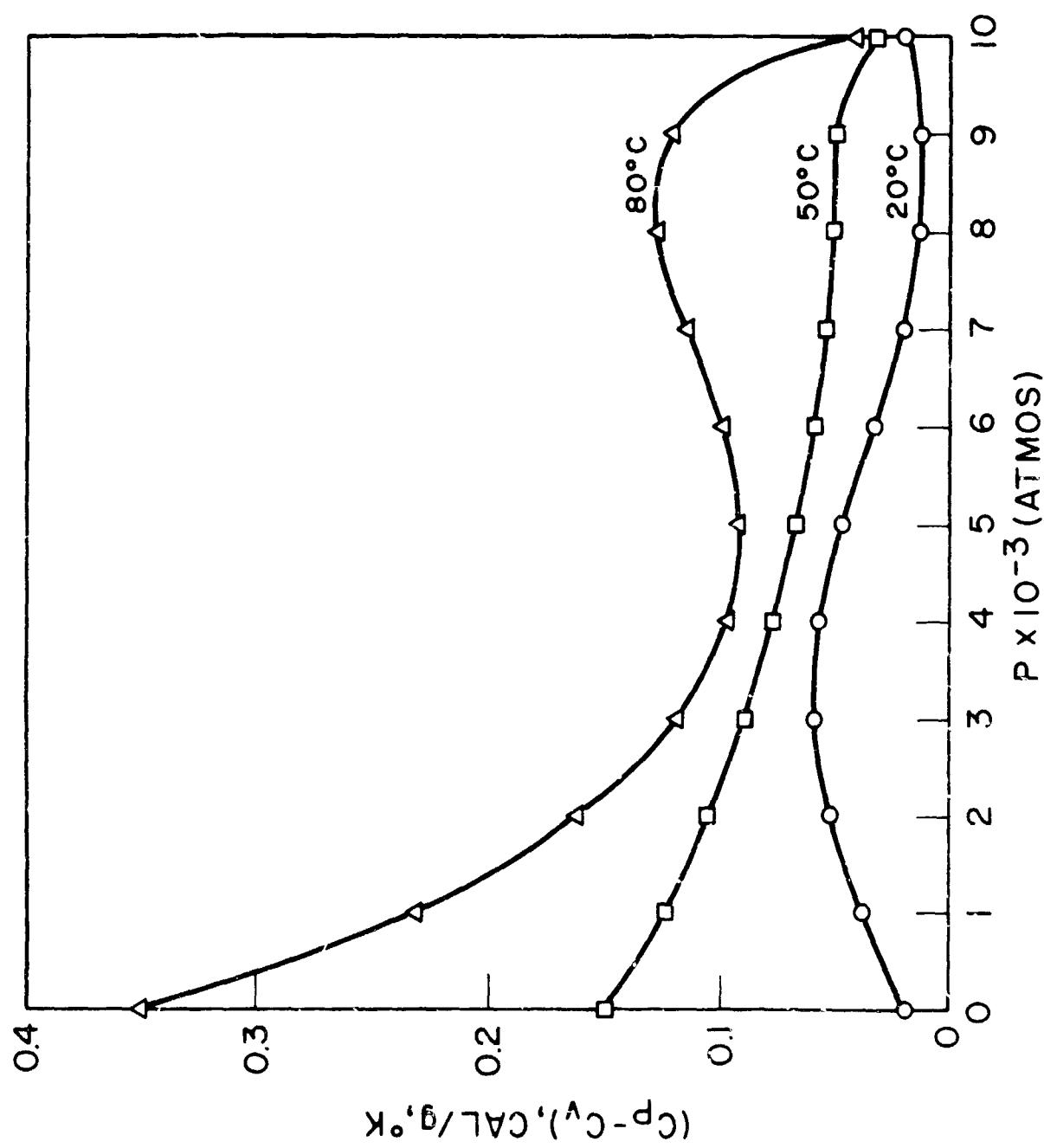
Figure 9. Pressure Dependence of $(C_p - C_v)$ of Polyethylene Along Isotherms
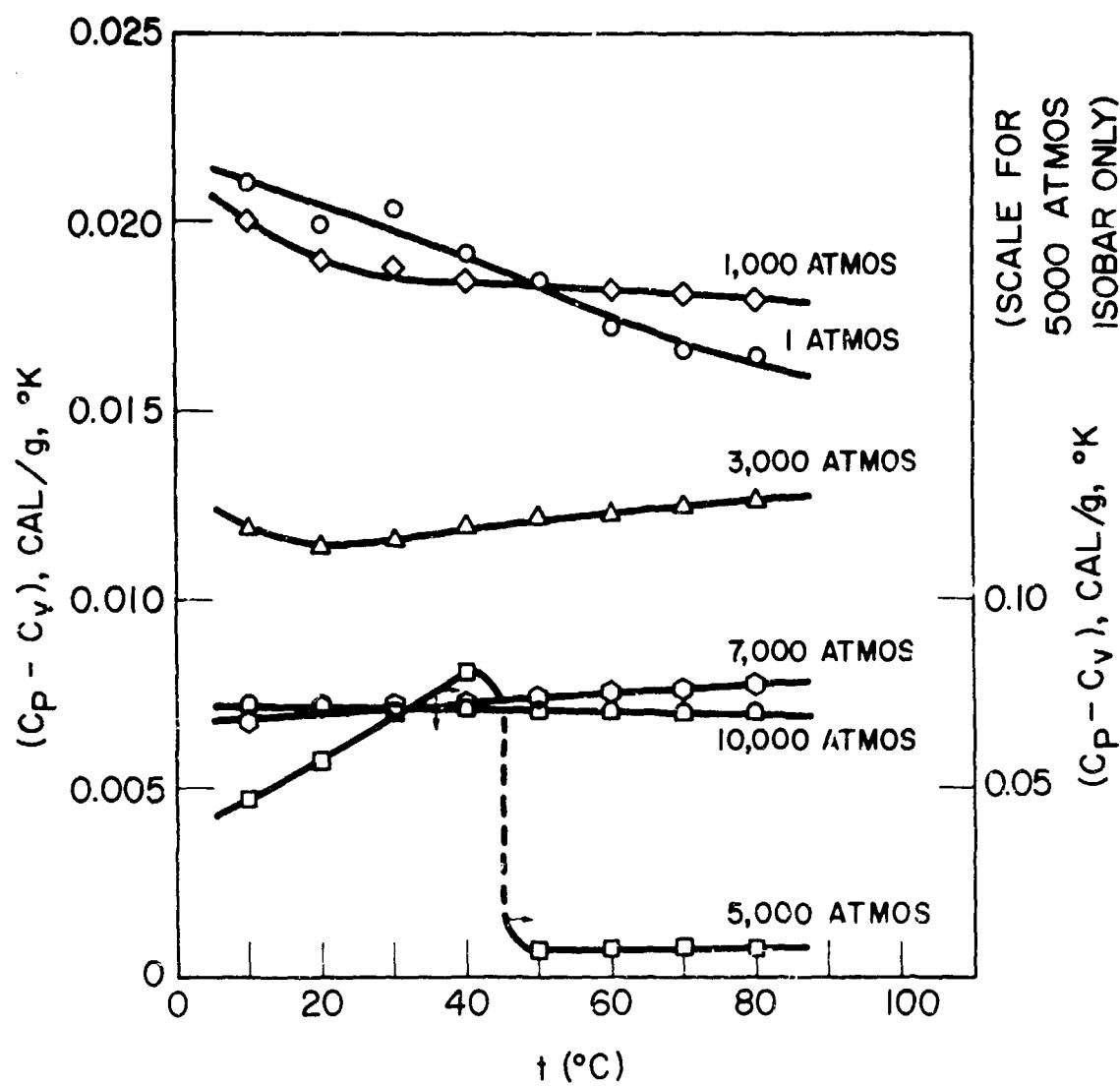
Figure 10. Temperature Dependence of $(C_p - C_v)$ of Polytetrafluoroethylene Along Isobars
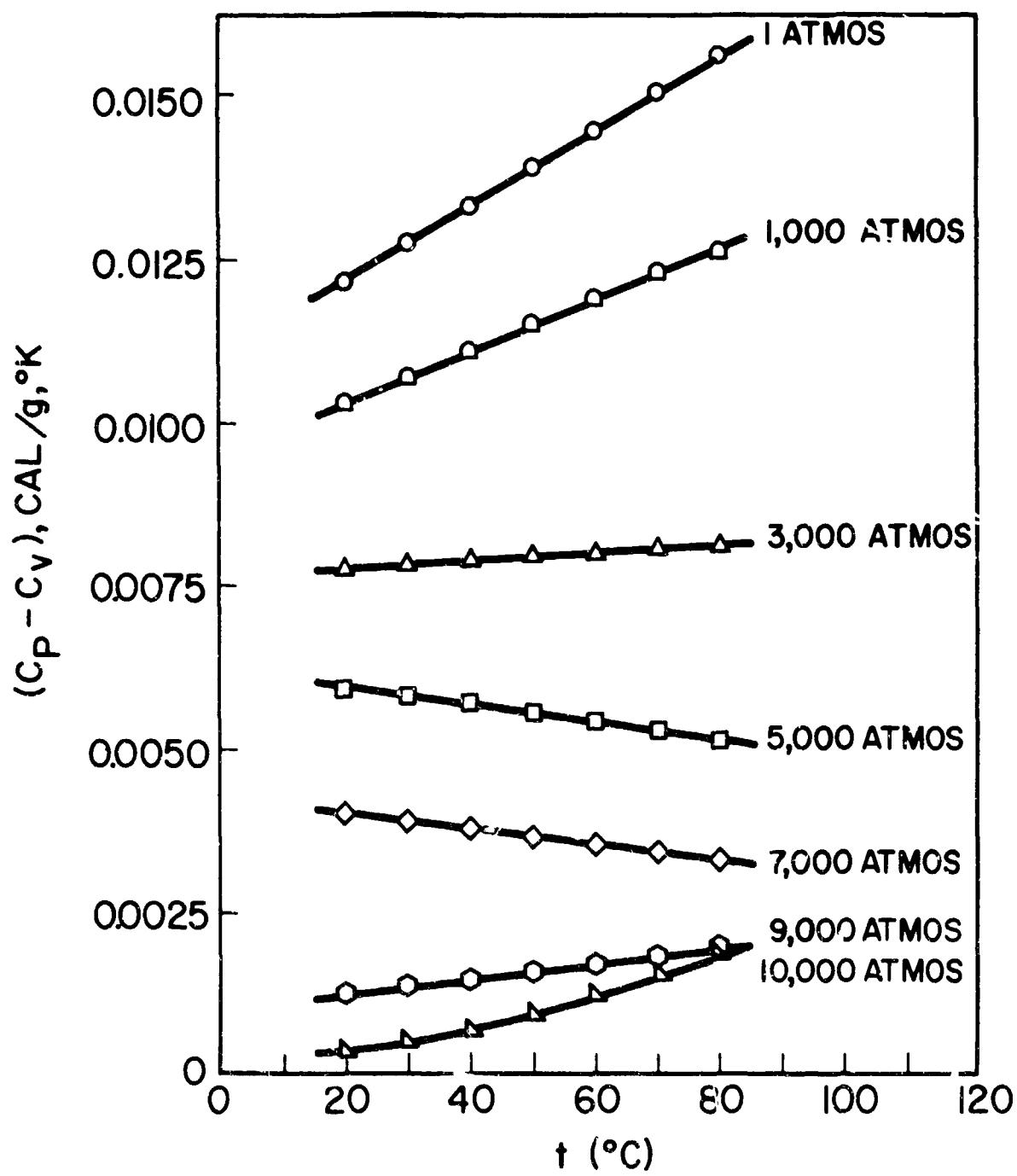
Figure 11. Temperature Dependence of $(C_p - C_v)$ of Polychlorotrifluoroethylene (Kel-F) Along Isobars
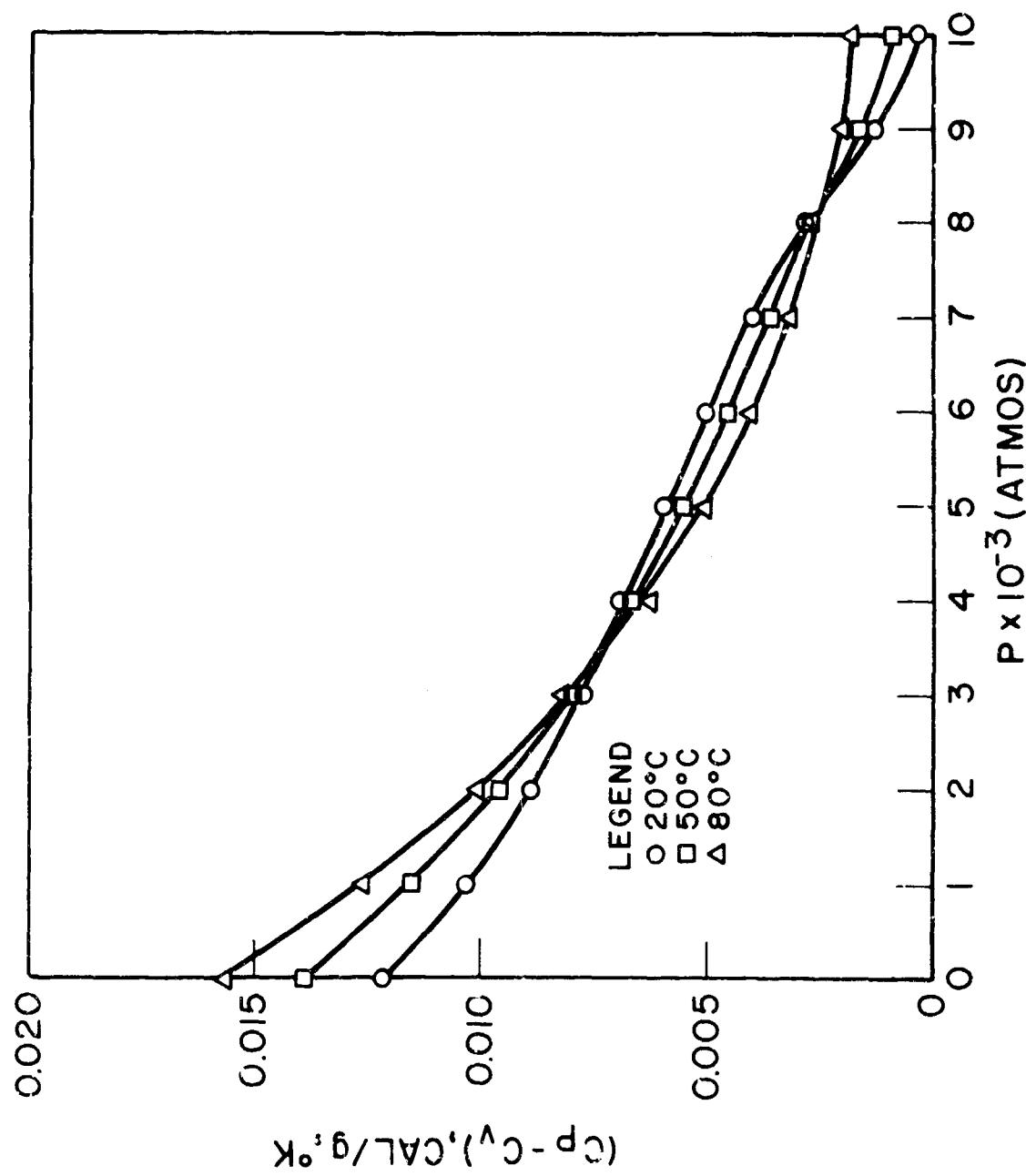
Figure 12. Pressure Dependence of $(C_P - C_v)$ of Polychlorotrifluoroethylene (Kel-F) Along Isotherms

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4. THE MIE-GRÜNEISEN EQUATION OF STATE

The thermal energy of crystalline materials consists of the vibrational energy of atoms in the lattice. The Grüneisen parameter can be expressed in terms of specific volume v and the frequency ν_i of the harmonic oscillators,

$$\Gamma = - (d \ln \nu / d \ln v)_{av}. \tag{8}$$

The Mie-Grüneisen equation of state may be written as:

$$P - P_0 = \Gamma (E - E_0) v \tag{9}$$

where P_0 and E_0 are pressure and energy of a reference state, and Γ is the Grüneisen parameter.

Differentiating P in Equation 9 with respect to E at constant volume and substituting $dE = C_v \, dT$, Γ can be expressed in terms of experimental quantities as:

$$\Gamma = v\alpha / C_v \beta \tag{10}$$

where α and β are the thermal expansion coefficient and the compressibility respectively. From equations of state and the experimental data discussed above, Γ can be easily calculated. The values of Γ for several polymers have been evaluated in Reference 1. Figures 13 and 14 present the Grüneisen parameter of Kel-F as functions of temperature and volume, respectively. The volume dependence of this parameter is well known, but the temperature dependence has not been clearly established. In the case of Kel-F in this limited temperature range, the Grüneisen parameter decreases significantly with temperature increase. Recently, Barker[24] has concluded that the Grüneisen parameter of polymers is ≈ 4 and the $d\Gamma/dT > 0$.

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Based on a simple model, Slater[25] has given an expression for the Grüneisen parameter as,

$$\Gamma = -2/3 - v(\partial^2 P/\partial v^2)_T/2(\partial P/\partial v)_T \tag{11}$$

This expression employs only the isothermal P-v property of a solid. This formula, as modified by Dougdale and McDonald, contains derivatives of $Pv^{2/3}$. It has recently been generalized by Al'tshuler[26], who gives

$$\Gamma = -(2/3-z/3) - v(\partial^2 Pv^{2z/3}/\partial v^2)/2(\partial Pv^{2z/3}/\partial v)_T \tag{12}$$

which includes the above two as special cases. The Slater theory corresponds to $z = 0$, and the Dougdale-McDonald theory corresponds to $z = 1$.

These formulas, which do not require calorimetric measurements, offer convenient means to obtain the Grüneisen parameter from any one of the three isothermal equations of state that have been fitted to the experimental data in this work. Based on Slater's theory, the expressions for the Grüneisen parameter from each of the three equations of state are given as follows:

Murnaghan Equation

$$\Gamma = (s - 1)/2 - 2/3 \tag{13}$$

Modified Birch Equation

$$\Gamma = -2/3 - (1/2B')\left[(B' + 2)(v/v_o)^{-1/B'} - (B' + 1)/2\right]\left[(v/v_o)^{-1/B'} - 1/2\right]^{-1} \tag{14}$$

or

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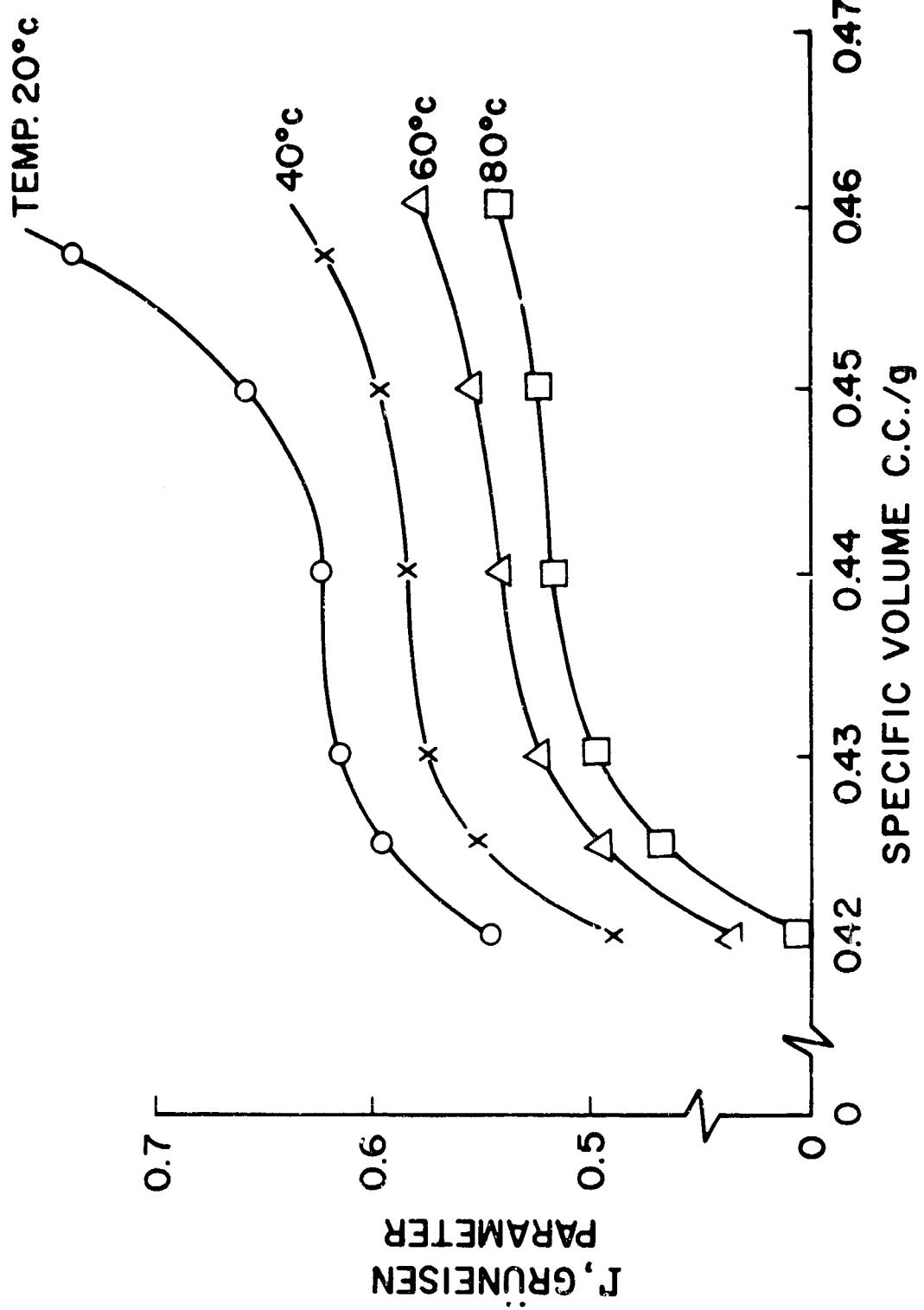
Figure 13.   Volume Dependence of the Grüneisen Parameter of Kel-F Along Isotherms

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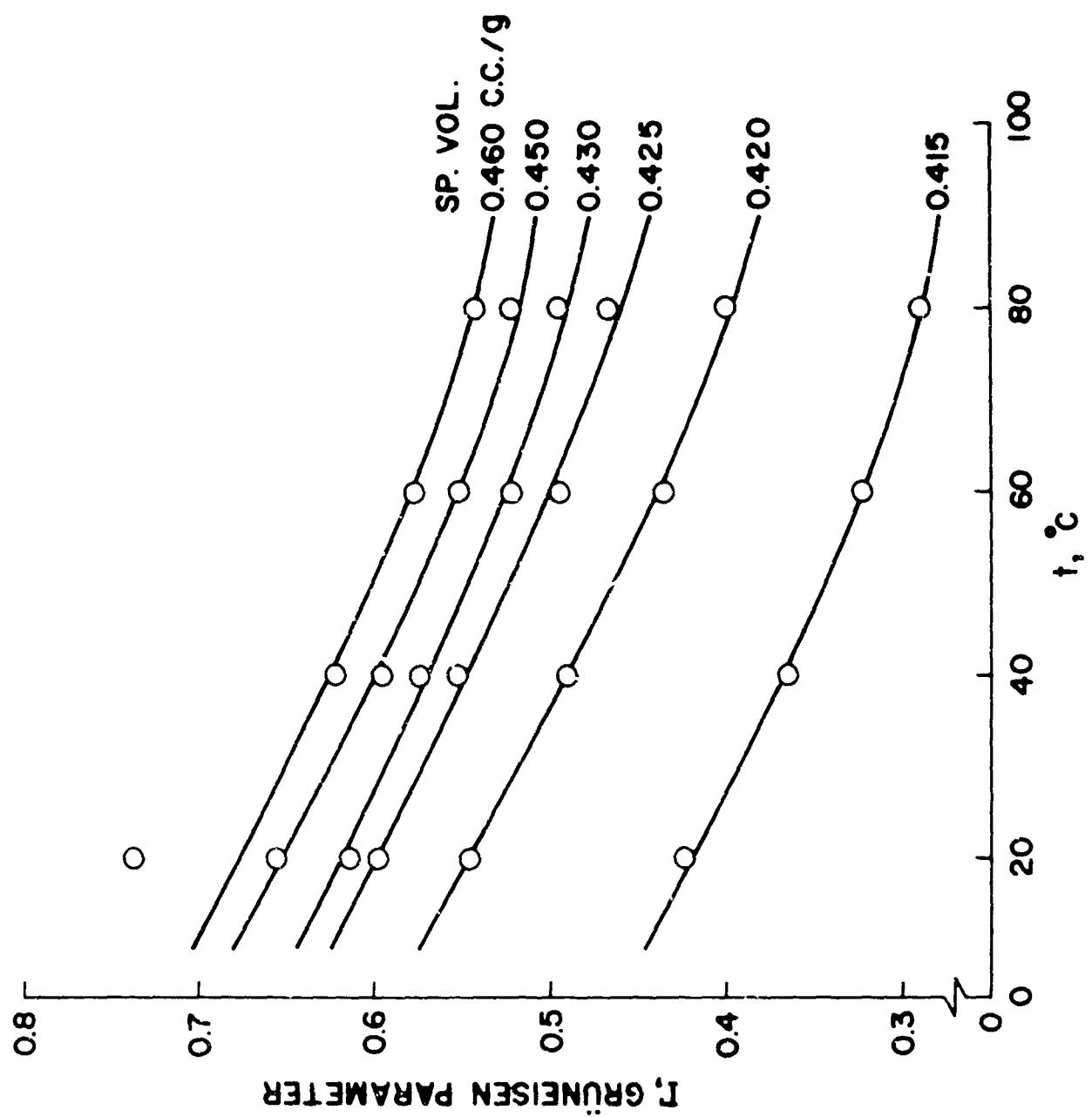
Figure 14. Temperature Dependence of the Grüneisen Parameters of Kel-F at Constant Volume

$$\Gamma = -2/3 + (1/4B')(P/A' + 1/4)^{-1/2} + (B' + 2)/2B' \tag{15}$$

Tait Equation

$$\Gamma = (v/v_0)/2A - 2/3 \tag{16}$$

The meanings of the parameters s, A', B' and A have been defined in Equation 2, Equation 4 and Equation 6.

In Equation 13, Γ is dependent only on s, which increases with increasing temperature in the cases of polymethyl methacrylate and polystyrene (Figure 1 and Figure 4). At lower temperatures, remote from the melting zone, Γ is in the order of 4.

In Equations 14 and 15, the dependence of Γ on volume or pressure is explicit, while the dependence on temperature is through A' and B'. Since the first factor $(2B')^{-1}$ is increasing with temperature (Figure 2), examination of the relative magnitudes of the terms in this equation shows that the derivative $d\Gamma/dT$ is positive for polymethylmethacrylate.

From Equation 16, the temperature derivative of the Grüneisen parameter is:

$$d\Gamma/dT = -(v/v_0)(dA/dT)/2A^2 - [dv/dT - (v/v_0)(dv_0/dT)](2Av_0)^{-1} \tag{17}$$

If the Tait parameter A is independent of temperature, $d\Gamma/dT > 0$ at high pressures because dv (P)/dT < dv$_0$ (P = 0)/dT. If $\wedge$ is decreasing with increasing temperature, as in the case of polymethylmethacrylate above 50°C (Figure 3), the first factor on the right-hand side of Equation 17 is also positive. If $A \approx 0.1$ and $dA/dT \approx [dv/dT - (v/v_0)(dv_0/dT)]$, the first term on the right-hand side of Equation 4-10 will be greater than the second term. Consequently, $d\Gamma/dT > 0$.

5. MELTING OF ORGANIC HIGH POLYMERS AT HIGH PRESSURES

The Simon equation has been used extensively to represent the melting temperature of solids as a function of melting pressure:

$$P_m - P_m^o = a \left[(T_m/T_m^o)^c - 1 \right] \tag{18}$$

where P_m (atmosphere) and T_m (^{o}K) are the melting pressure and temperature respectively. If $P_m^o = 1$ is taken as reference pressure, then T_m^o is the melting point of the solid at 1 atmosphere.

The melting temperature of polymers increase with pressure as is the case of other solids. On the other hand, the melting zone of high polymers covers a rather large temperature range. The amorphous constituent softens gradually, and the crystallites of increasing size melt at progressively higher temperatures.

The melting transition zone of polystyrene (atactic, amorphous), polyvinyl chloride, polymethyl methacrylate, and two types of polyethylene (high and low densities) has been investigated by Hellwege et al.[6] under pressures up to 2000 Kg/cm^2. The melting of several types of polyethylene under pressures up to 4,000 atmospheres has been investigated by Matsuoka[27]. The melting of a type of high density polyethylene has been studied by Osugi and Hara[28] up to 30,000 atmospheres where the melting temperature is 400°C. McGeer and Duus[29] obtained data on the melting of Teflon under pressures up to 615 atmospheres.

Based on these results, the parameters for polymers in the Simon's equation have been evaluated. These parameters are presented in Table 7. A list of the Simon constants for solid elements and compounds has been given by Babb[30]. The constants for polymers presented in Table 7 are comparable with those for some of the solids studied by Babb.

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Table 7. Parameters of the Simon Equation for Polymers

Polymer	a (atm)	c	Pressure Range (atm)
Teflon	1086	3.329	1 to 615
Polystyrene	19961	0.5928	1 to 2000
Low Density Polyethylene	4369	3.261	1 to 4000
High Density Polyethylene (Marlex 9)	6742	2.115	1 to 2000
High Density Polyethylene (Marlex 50)	3100	4.5	1 to 30,000*
Polyvinyl Chloride (Hart)	18869	1.27	1 to 2000
Polymethyl Methacrylate	7526	2.083	1 to 1500

* J. Osugi and K. Hara Rev. Phys. Chem.(Japan) 36, 28, 1966

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Salter has pointed out that the Simon constant c is related to the Grüneisen parameter by the following equation:

$$c = (\Gamma + 1/6)(\Gamma - 1/3)^{-1}{}^{(41)} \qquad (19)$$

which would enable theoretical calculation of c if the Grüneisen parameter is known more accurately.

Recently, Kennedy[31] has discovered empirically that the melting temperature T_m is a linear function of the isothermal compression $(\Delta v/v_o)$ at normal temperature:

$$t_m(P) = t_m^o (1 + k \Delta v/v_o), \, {}^{o}C \qquad (20)$$

In subsequent articles[32 and 33] Kennedy et al. have shown that for the majority of solids Equation 20 holds very well. For a few solids, such as solid argon and methane, the deviations observed might be attributable to quantum effects or the uncertainties in the compression.

Gilvarry[34] and Vaidya and Gopal[35] have derived the relations between the constant k in Equation 20 and the Grüneisen parameter Γ, and between k and the constant c in Simon Equation:

$$k = 2(\Gamma - 1/3) = (c - 1)^{-1} \qquad (21)$$

The available melting data of polymers have been assembled to test the Kennedy's fusion equation. Within the range of the available data, Equation 20 seems to be applicable to polymers. The results for six polymers are plotted in Figure 15, and the constant k is presented in Table 8. The compression data for polytetrafluoroethylene and low density polyethylene were based on the data by Weir[5]. Both the melting and the compression data of polystyrene, polyvinyl chloride, and polymethyl methacrylate were based on the data of Hellwege et al.[6].

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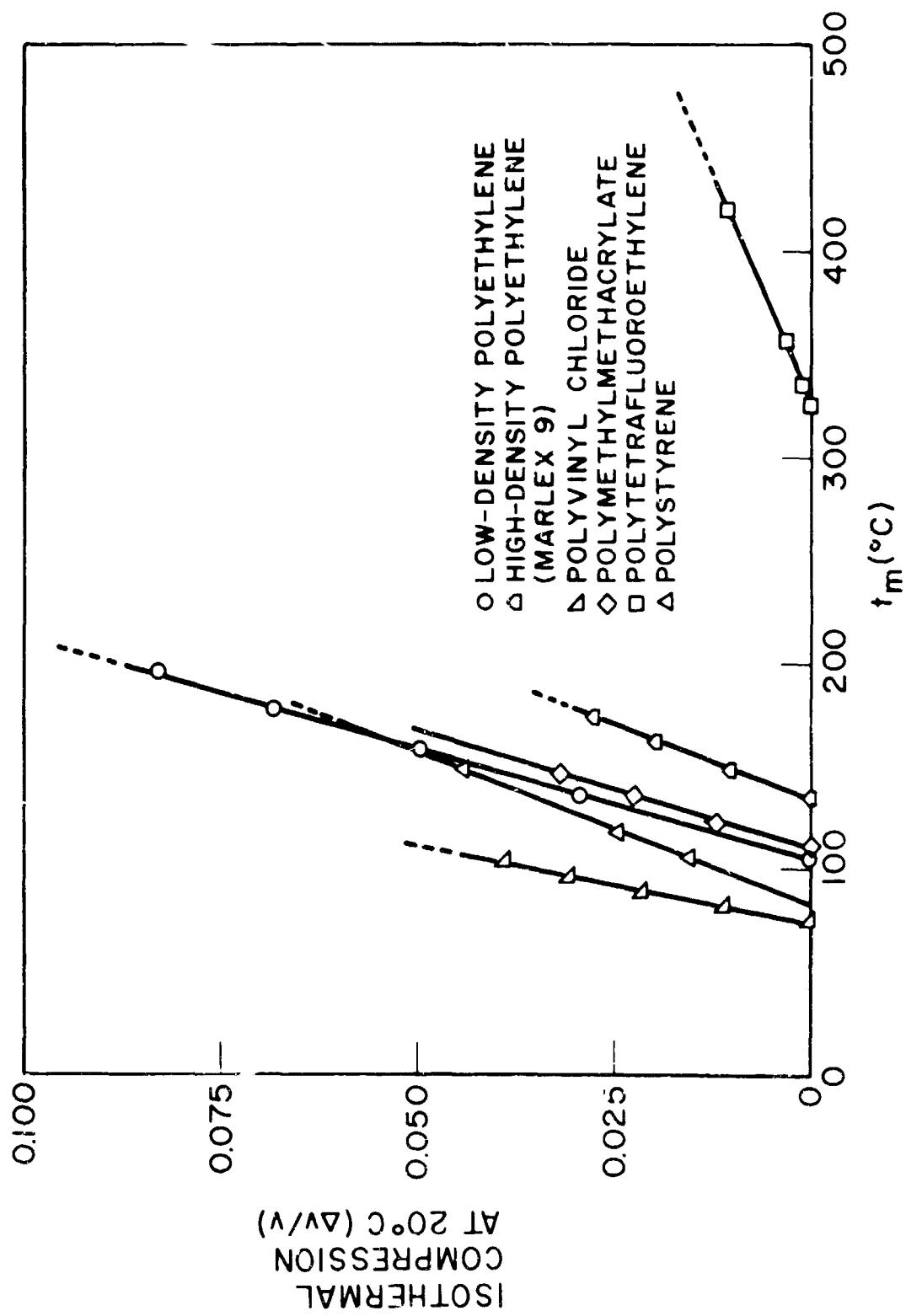
Figure 15. Application of the Kennedy Fusion Law to Organic High Polymers

Table 8. Constants in the Kennedy Fusion Equation

Polymer	k	t_m (°C)	Maximum $\Delta v / v_0$
Polytetrafluoro-ethylene	26.78	325	0.0108
Low Density Polyethylene	9.27	110	0.0829
High Density Polyethylene (Marlex 9)	10.33	136	0.0276
Polystyrene	19.75	79.6*	0.0441
Polyvinyl Chloride (Hart)	11.02	71.5	0.0395
Polymethyl Methacrylate	11.02	108.1	0.0319

*Value obtained by extrapolation to 1 atmosphere

By combining Equation 20 with the isothermal equations of state, the melting temperature can be directly predicted. The melting temperature of high density polyethylene (Marlex 50) measured by Osugi and Hara[28] at pressures up to 30,000 atmospheres is compared with the calculated melting temperature by means of Equation 20 in Table 9. The compression $\Delta v/v_o$ was calculated from the isothermal equations of state Equations 2, 3, and 6. The constant k in Table 8, and the constants in these equations were determined for pressures up to 2000 Kg/cm^2 for Marlex 9 which is different from Marlex 50 in the degree of crystallinity and the number of methyl groups (CH_3) per 100 carbon atoms. Below 10,000 atmospheres, all those equations yield values agreeing with the experimental data within 1 percent. Above 10,000 atmospheres the difference between the calculated and experimental melting temperature is greater. Both the Birch and the Tait equations give values which deviate from the experimental by less than 10 percent at 30,000 atmospheres. The value from the Murnaghan equation differs slightly more, 10.2 percent, at 30,000 atmospheres.

Table 9. Comparison of Measured and Predicted Melting Temperature
of High Density P   ylene by Means of Isothermal Equations of
State and Kennedy Fusion Law

Pm, Atm	T_m, ^{o}K (Measured)	Predicted T_m, ^{o}K		
		Birch Eq	Murnaghan Eq.	Tait Eq
1	409	409	409	409
1,000	431	437	437	437
3,000	468	474	472	473
5,000	509	501	494	498
10,000	551	545	529	539
20,000	630	597	567	585
30,000	671	630	590	613

6. SHOCK COMPRESSION OF HIGH POLYMERS

Shock compression is a means of obtaining semi-empirical equations of state for matter
under high pressures and high temperatures. Properties of matter under such conditions
are determined by the interactions and thermal vibrations of its component molecules, atoms,
ions, and the excitation of the electrons. Static compression under isothermal conditions
serves to investigate the forces of interaction, and the thermal energy at the prevailing
temperature. For a given initial state, the isothermal pressure can be calculated for a
specified volume, v, by use of the isothermal equations of state developed above. If the
pressure due to temperature rise can be determined, then the prediction of the shock
compression curve, better known as Hugoniot, is possible.

In a general non-isothermal compression,

$$dP = (\partial P/\partial v)_T \, dv + (\partial P/\partial T)_v \, dT \tag{22}$$

with use of the well known relations

$$(\partial P/\partial T) = - (\partial \ln v/\partial T)_P / (\partial \ln v/\partial P)_T$$

Equation 6-1 can be rearranged to give

$$-dP/v (\partial P/\partial v)_T = - dv/v + (\partial \ln v/\partial T)_P \, dT \tag{23}$$

Integration of Equation 23 will be easy if the thermal expansion coefficient $\alpha = (\partial \ln v/\partial T)_P$
is assumed constant. It has been shown[1], based on such an assumption of constant α, that
a non-isothermal Murnaghan Equation can be derived,

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$$P = (B_0/s) [(v_0/v)^s - 1] + B_0 (v_0/v)^s \alpha (T - T_0) \tag{24}$$

where B_0 and s are the parameters in the Murnaghan Equation of state and the other symbols have the usual meanings. By equating the Rankine-Hugoniot Equation to the integrated internal energy,

$$\int_{E_0}^{E} dE = \int_{T_0}^{T} C_v \, dT + \int_{v_0}^{v} [T \, (\partial P/\partial T)_v - P] \, dv$$

The Hugoniot pressure can be expressed as,

$$P_H = P_0 + [g(x)/C_v] [P_0 v_0 (1 - 1/x) - F(x)] [1 - v_0 (1 - 1/x) g(x)/2C_v]^{-1} \tag{25}$$

where P_H is the Hugoniot pressure and P_0 is the isothermal pressure at the same volume ratios v_0/v. The other quantities are defined below

$$x = v_0/v$$

$$g(x) = B_0 \alpha x^s$$

$$F(x) = B_0 v_0 [(1 - s \alpha T_0) (x^{s-1} - 1)/s (s - 1) - (1 - 1/x)/s]$$

Equation 25 is based on the Murnaghan Equation. The Birch and Tait Equations can also be employed in such derivations, but the Murnaghan Equation gives the simplest expression for P_H.

The shock compression data for several vinyl polymers are available[36]; however, except for density, other characteristics of the polymers used in those experiments and the initial

conditions in the experiments are not known. In order to use Equation 25, one must select constants in the Murnaghan equation for the given material and given initial temperature of the shock experiment.

It is stated[36], that the material used in the shock compression of polychlorotrifluoroethylene (Kel-F) has an initial density ρ_o = 2.1, but the initial temperature of the experiment is not given. For this density the specific volume is 0.4762 cm^3/g. The data of Weir[5] and Hoffman and Weeks[23] indicate that this material has a degree of crystallinity of about 26 percent. Using the data in Reference 23 and Reference 5, degree of crystallinity is calculated for a series of specific volumes. With this information, the parameters in the Murnaghan Equation as functions of crystallinity can be plotted and extrapolated to the degree of crystallinity of the test sample. Thus, the Murnaghan parameters s and B_o are obtained as 7.4 and 10,761 atmospheres, respectively.

In the case of plexiglas (it is assumed to be polymethylmethacrylate), the ρ_o given was 1.18 g/c.c., corresponding to a specific volume of 0.8475 cm^3/g. By use of the specific volume as a function of temperature at one atmosphere reported by Hellwege et al.[6], it is estimated that this ρ_o corresponds to a temperature of 42.5^{o}C (108.5^{o}F). From Figure 1 the parameters s and B_o for the Murnaghan Equation are found to be 8.70 and 35,550 Kg/cm^2, respectively.

In Reference 36, it is stated that the polyethylene used in a shock compression test has a density of 0.92 g/c.c. Three materials of the same density (0.92 g/c.c.) and differing molecular weight, between 14,000 and 38,000 (determined by viscosity), was used by Bridgman[10] for static compression to 40,000 Kg/cm^2. The branched polyethylene used by Weir[5] has a density of 0.918 g/c.c. at 20°C. A high pressure polyethylene with a density of 0.918 g/c.c. at 20°C was also used by Hellwege et al. However, it is evident from Figure 16 that the pressure versus v_o/v curves for all static compression lie above that for the shock compression test. For a given material, however, this situation is thermo-dynamically impossible. This seems to indicate that a material of much higher compressibility

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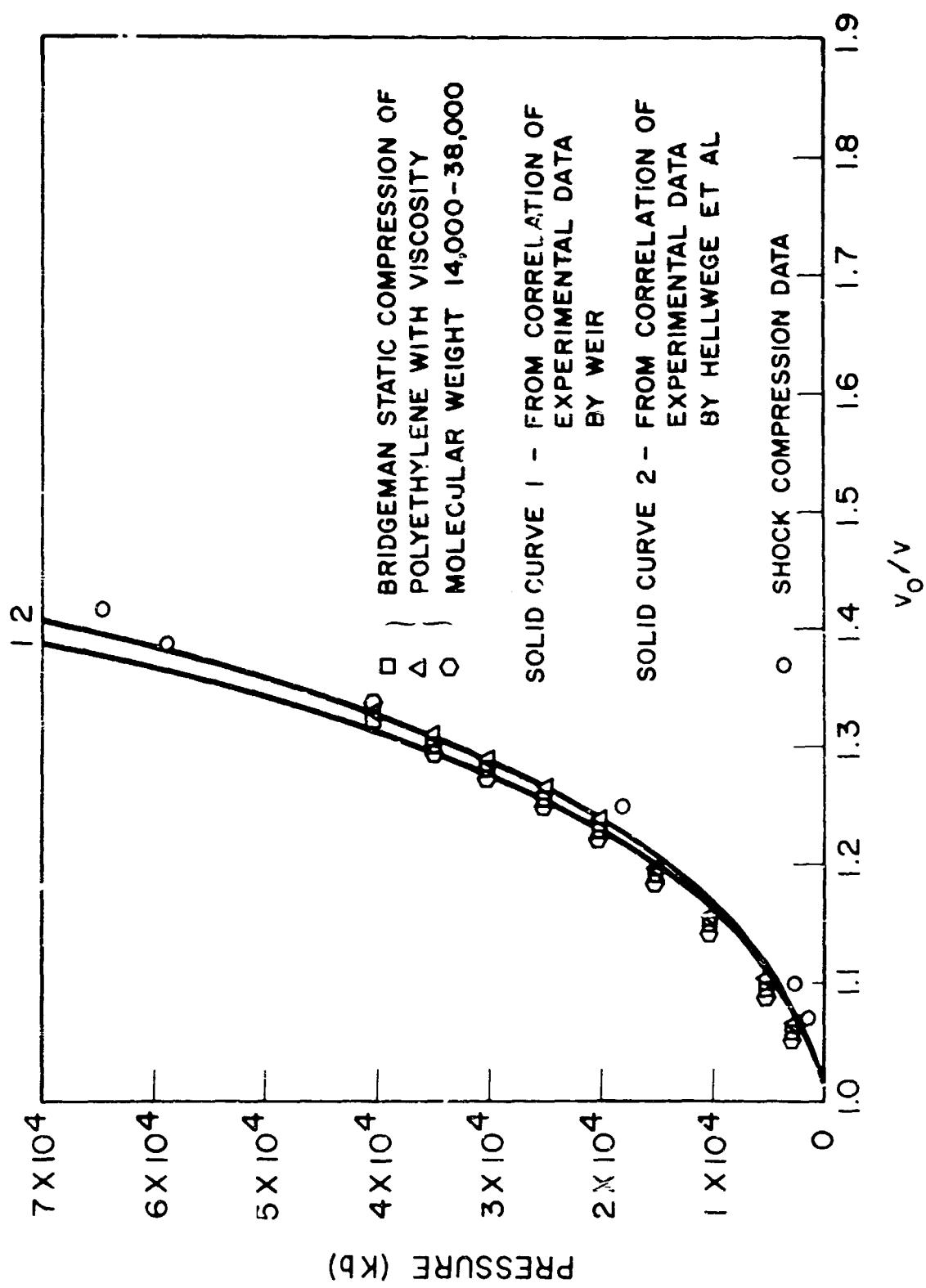
Figure 16. Comparison of Static Compression and Shock Compression of Low Density Polyethylene

has been used in the shock experiment, or the ambient temperature at the site of experiment is much higher than the temperature at which the density was measured.

7. DISCUSSION AND CONCLUSIONS

The results of our recent interest in the equations of state of high polymers has been reported. Adoption of the semi-empirical equations of state for solids for use with polymers seems to have a wide range of applicability. The results presented in this paper indicate that they are capable of predicting the isothermal volumetric data with good accuracy to very high pressures. They give smooth and reasonable values for the first and second derivatives. The compressibility of polymers calculated from these equations are quite close to the values obtained from graphically determined slopes and the values calculated from empirical polynomial equations.

The ability of these equations to predict static data (Table 5) at high pressures much beyond the original data range is quite impressive. The data calculated to 40,000 Kg/cm^2 in Table 5 were based on constants which were obtained from the data of Hellwege et al. up to only 2000 Kg/cm^2.

By use of the theory of Slater[25] or the generalized theory by Al'tshuler[26], the Grüneisen parameters can be obtained from these equations. The Murnaghan Equation yields Grüneisen parameters dependent only on temperature; while the Tait and generalized Birch equations both predict Grüneisen parameters dependent on both volume and temperature. The values thus predicted seem to possess the correct theoretical magnitude at normal temperatures.

When combined with the Kennedy fusion law, these equations predict the melting temperatures of polyethylene (Table 9) to within 10 percent at pressures more than fifteen times the original pressure range.

Under shock compression, the temperature is very high but the polymers remain solid because of the high melting point under pressure. Normalization of the temperature scale by the melting temperature may extend the range of applicability of the parameters in the equations of state to the solid in this high temperature, high pressure region.

The range of applicability and the accuracy of these equations of state may be enhanced if they are fitted to accurately measured compressibility or bulk modulus data rather than specific volume data. As proposed by Anderson [2, 37] measurements of ultrasonic speed in materials under high pressure is most suitable for obtaining accurate compressibility $[- (\partial \ln v / \partial P)_T]$ or bulk modulus $[- (\partial P / \partial \ln v)_T]$ data. The compressibility of polymers has values in the order of 10^{-5} which cannot be obtained accurately from direct volumetric measurements. Since the compressibility is the first derivative of $(\ln v)$ with respect to P, accurate values of specific volume can be obtained by integrating the compressibility data. From such data, accurate values of thermal expansion coefficient of polymers, which is in the order of 10^{-4}, can also be obtained.

Guenther et al. [38] have measured the ultrasonic speed in polymers as a function of temperature under atmospheric pressure. Zosui [39] measured the ultrasonic speed in polyvinylchloride at 1 atmosphere and 1000 atmospheres from $20^{o}C$ to $140^{o}C$. If accurate values of C_v are available, accurate values of compressibility under atmospheric pressure can be obtained as a function of temperature from Reference (38). A more detailed description and specification of the polymers and the initial conditions of the experiment other than just a statement of the density would be valuable for theoretical work.

The success of applying to polymers the semi empirical equations based on finite strain theory, may be attributable to the increase in degree of crystallinity in polymers under high pressure. Although the Tait equation has no theoretical basis, it nevertheless gives a bulk modulus very close to the values calculated from the other two equations. The Tait Equation constant A was found to vary with temperature. This variation becomes large

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when the melting point is approached (Figure 3). It is speculated that the Murnaghan parameter, s, and the parameter a_2 in the generalized Birch equation may also be nearly universal constants for a wide range of materials.

In shock compression, temperature rises with pressure. Degree of crystallinity of polymers increases with pressure[3,40] but decreases with increasing temperature[12,23]. At low temperatures, the degree of crystallinity decreases very slowly with increasing temperature. As the melting temperature is approached, the degree of crystallinity drops rapidly to zero at the melting point. In this region, the rate of increasing crystallinity produced by pressure may become insignificant in comparison to the rapid decrease of crystallinity produced by temperature. This situation may account for the decrease in slope of the Hugoniots at the highest shock pressures.

ACKNOWLEDGMENT

NOMENCLATURE

A   Tait Equation Parameter, Dimensionless.

A'   Defined in Equation (4).

a   Constant in the Simon Equation, Equation (18).

a_2 Constant in the generalized Birch Equation, Equation (3).

B_0 Constant in the Murnaghan Equation, Equation (2), atm., or Kg/cm^2.

B   Bulk modulus defined as $-v\, (\partial p/\partial v)_T$; Constant in the Tait Equation.

B'   Defined in Equation (4).

c   Constant in the Simon Equation, Equation (18).

C_P Specific heat at constant pressure, cal/g, $^{\circ}K$.

C_v Specific heat at constant volume, cal/g, $^{\circ}K$.

E   Internal energy.

E_0 Internal energy at a reference state.

F(x)   Defined in Equation (25).

$g(x)$	Defined in Equation (25).
K_0	Constant in the generalized Birch Equation, Equation (3), atm., or Kg/cm^2.
k	Constant in the Kennedy fusion equation, Equation (20).
P_H	Hugoniot pressure, atm., Equation (25).
P_0	Pressure of a reference state, a'm., Equation (9).
P	Pressure, atm.
P_m, P_m^0	Melting pressure, and reference melting pressure, usually 1 atm.
s	Constant in the Murnaghan Equation, dimensionless.
T	Temperature, $^\circ K$.
t	Temperature, $^\circ C$.
Tm, tm, T_m^0, t_m^0	Melting temperature, and reference melting temperature.
T_0	Reference temperature, $^\circ K$.
v	Specific volume, cm^3/g, under pressure P.
v_0	Initial specific volume, at 1 atm.
x	Defined as (v_0/v).
z	Defined in Equation (12).

GREEK SYMBOLS

α Thermal expansion coefficient, defined as $(\partial \ln v / \partial T)$ $(^{\circ}K)^{-1}$

β Compressibility, defined as $-v^{-1}(\partial v/\partial p)_T$, atm^{-1}.

Γ Grüneisen parameter defined in Equation (8) and Equation (9).

ν Frequency of harmonic oscillators, cps.

ρ Density at a reference temperature, T_o,

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